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Agata Szygula, Guibal Eric, María Ariño Palacín, Montserrat Ruiz, Ana Maria Sastre. Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan. *Journal of Environmental Management*, 2009, 90 (10), pp.2979-2986. 10.1016/j.jenvman.2009.04.002 . hal-04663102

HAL Id: hal-04663102

<https://imt-mines-ales.hal.science/hal-04663102v1>

Submitted on 27 Jan 2025

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Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan

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A B S T R A C T

Chitosan (a biopolymer) is an aminopolysaccharide that can be used for the treatment of colored solutions by coagulation–flocculation (as an alternative to more conventional processes such as sorption). Acid Blue 92 (a sulfonic dye) was selected as a model dye for verifying chitosan's ability to treat textile wastewater. A preliminary experiment demonstrated that chitosan was more efficient at color removal in tap water than in demineralized water, and that a substantially lower concentration of chitosan could be used with tap water. Dye removal reached up to 99% under optimum concentration; i.e., in terms of the acidic solutions and the stoichiometric ratio between the amine groups of the biopolymer and the sulfonic groups in the dye. The flocs were recovered and the dye was efficiently removed using alkaline solutions (0.001–1 M NaOH solutions) and the biopolymer, re-dissolved in acetic acid solution, was reused in a further treatment cycle.

Keywords:

Dye
Coagulation–flocculation
Chitosan
Acid Blue 92
Tap water

1. Introduction

Water is a scarce resource. Only 0.03% of the world's water reserves are available for human activities. Population growth and industrial booms have increased demand for water, while supply has remained constant. Moreover, inappropriate water management has reduced the amount of available resources (Allegre et al., 2004). In the textile industry, regulations concerning the discharge of wastewaters have become more and more stringent (Prigione et al., 2007). A number of processes have been tested for the decolorization of textile waters, including (a) sorption on activated carbon (Kavitha and Namasivayam, 2008) or biosorbents (O'Mahony et al., 2002), (b) oxidation and photo-oxidation (Muruganandham and Swaminathan, 2007), (c) chemical treatment (Gao et al., 2007), and (d) coagulation–flocculation (Somasundaran and Runkana, 2005; Zeng et al., 2007; Koprivanac et al., 2000). The coagulation–flocculation process can be used as a pre-treatment, a post-treatment or even a main treatment (Dos Santos et al., 2007; Gähr et al., 1994). This process is cost-effective, is easy to use and consumes less energy than alternative treatments (Choi et al., 2001; Chu, 2001). A number of coagulants are commercially

available, but some of them have received attention for their potential health impacts (Divakaran and Pillai, 2001). For example, the use of inorganic salts, such as aluminum chloride or aluminum sulfate, is now controversial due to their possible contribution to Alzheimer's disease. Polyacrylamide-based materials are also frequently used; however, the possible release of monomers is now considered harmful because they can enter the food chain, causing potential health impacts (e.g., carcinogenic effects) (Roussy et al., 2005a). The increasing demand for environmentally friendly technologies has sparked interest in natural polyelectrolytes, which can replace synthetic flocculants. Natural coagulants extracted from waste can serve as alternatives to synthetic polyelectrolytes because they are biodegradable, are safe for human health, and have a wider effective dosage range for flocculation of colloidal suspensions (Sanghi et al., 2006). Since most natural colloids are negatively charged, cationic polyelectrolytes are of particular interest as potential flocculants. The most promising cationic biopolymer for extensive application is chitosan (Bratskaya et al., 2004). Chitosan is an aminopolysaccharide extracted by means of deacetylation from chitin, one of the most abundant biopolymers in nature after cellulose (Ruiz et al., 2000, 2001; Gibbs et al., 2003). Chitosan has been studied for use as a coagulant or flocculant for a wide variety of applications, including fish processing (Guerrero et al., 1998), the food industry (Chi and Cheng, 2006), silt in river water (Divakaran and Pillai, 2002), latex particles (Ashmore and

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Hearn, 2000), microorganisms (Barany and Szepesszentgyorgyi, 2004), and mineral colloids (Roussy et al., 2004). The protonation of amine groups in acidic media (with the remarkable exception of sulfuric acid solutions) causes chitosan to dissolve. The solubility properties of chitosan are controlled by a series of parameters such as molecular weight (Guibal, 2005), degree of deacetylation (Sorlier et al., 2001) and ionic composition of the solution (Roberts, 1992). Chitosan that was initially dissolved in acid media can precipitate when diluted into alkaline solutions (Roussy et al., 2005b). The mechanisms involved in the coagulation–flocculation of suspended matter and colloids include charge neutralization (Bolto and Gregory, 2007), bridging (Bolto, 1995) and electrostatic patch (Gregory, 1973). Despite extensive knowledge of the mechanisms involved in the interactions between chitosan and dissolved or suspended matter, it is generally difficult to predict optimum operational parameters, and in most cases a preliminary experimental study is required in order to verify the stoichiometry that may exist between chitosan and dye molecules (Al Mubaddal et al., 2007).

This study examines the coagulation–flocculation of a model dye (Acid Blue 92, AB92) using chitosan as a coagulant–flocculant. The experimental procedure considered the effect of the initial pH and the dye concentration in order to evaluate the optimum molar ratio between the amine groups (of chitosan) and the sulfonic groups (of AB92) at biopolymer saturation. The last section of this paper describes the removal of the dye from flocs using alkaline solutions. The possibility of recycling the chitosan (after dye removal and re-dissolving) was also considered.

2. Materials and methods

2.1. Chitosan

Chitosan was supplied by Aber Technologies (Plouvien, France). Its degree of deacetylation was determined by Fourier transform infrared (FTIR) spectroscopy (Guibal et al., 1999). The molecular weight (MW) was measured by size exclusion chromatography (SEC) coupled with light scattering and refractometry (Ruiz et al., 2001). The chitosan's degree of deacetylation was found to be 87% and its MW_n was found to be $125,000 \text{ g mol}^{-1}$. It was ground and sieved, after which the 0–125 μm size fraction was collected and used to prepare the coagulant solutions. In order to facilitate the preparation of the polymer solutions, the chitosan (1 g) was hydrated overnight in demineralized water (98 mL), after which 1 g of acetic acid solution (80% w/w) was added under agitation. The solution was left to settle overnight before being used. The final pH was close to 4. The mean water content in the chitosan samples was

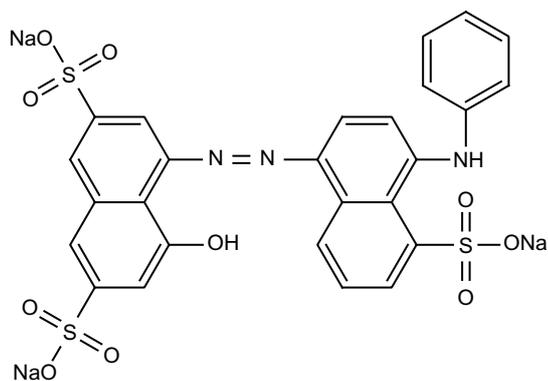


Fig. 1. Chemical structure of AB92.

Table 1
Main characteristics of tap water.

Parameter	
Ca ²⁺	42 mg L ⁻¹
Mg ²⁺	20 mg L ⁻¹
K ⁺	2 mg L ⁻¹
Na ⁺	24 mg L ⁻¹
NO ₃ ⁻	3.4 mg L ⁻¹
HCO ₃ ⁻	140 mg L ⁻¹
Cl ⁻	9 mg L ⁻¹
SO ₄ ²⁻	120 mg L ⁻¹
pH	7.7
Ionic conductivity	550 $\mu\text{S cm}^{-1}$

close to 10%, and this percentage was taken into account when calculating the true concentrations.

2.2. Dye

AB92 (anazoline sodium, C₂₆H₁₆N₃Na₃O₁₀S₃) was supplied by Sigma-Aldrich (Spain) (CI number 13390) and was used without purification. The product is a commercial salt consisting of a mixture of dye and an inert product; the true dye content was 40%. This dye purity was taken into account in calculating the concentrations. Fig. 1 shows the chemical structure of the dye. The

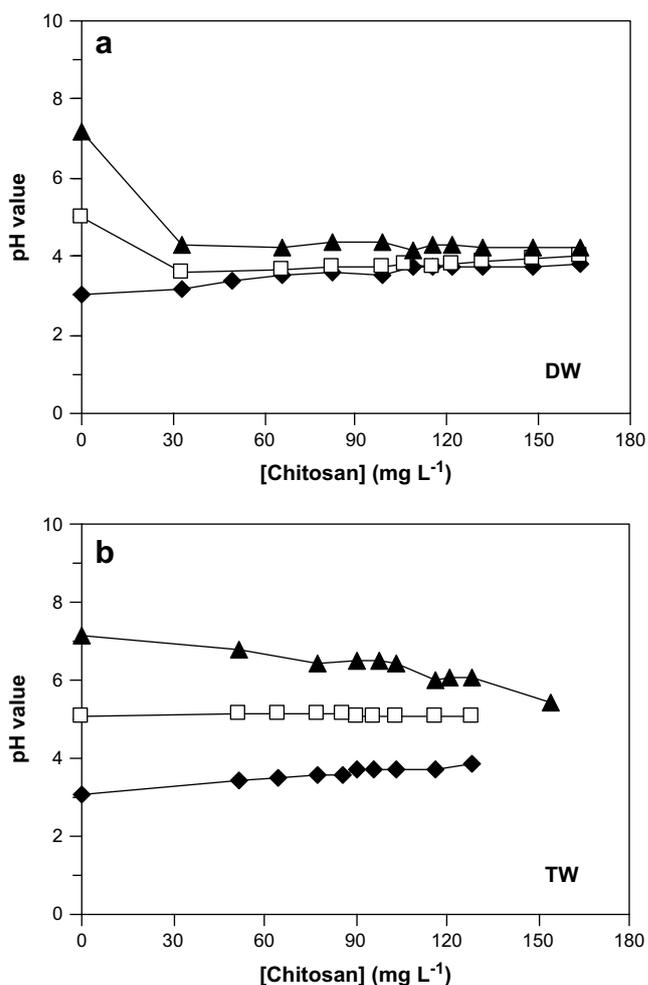


Fig. 2. Effect of chitosan dosage on the final pH of dye solutions prepared with (a) demineralized water (DW) and (b) tap water (TW). Dye concentration: 100 mg L^{-1} .

MW of the dye was $695.58 \text{ g mol}^{-1}$. AB92 is a monoazo compound bearing three sulfonic groups; it holds negative charges in aqueous solutions. Dye solutions were prepared by means of direct dilution in water (at the appropriate concentration) and the pH was controlled with hydrochloric acid and sodium hydroxide solutions.

The dye concentration was measured by means of UV-visible spectrophotometry (Shimadzu UV-1650, Japan) at a wavelength of 594 nm after pH control. Since the dye spectrum may be affected by the pH of the solution, a drop of concentrated H_2SO_4 solution was, for analytical purposes, systematically added to the samples (after filtration) in order to ensure a constant pH. The dye solutions were prepared with demineralized or tap water, depending on the experiment. Table 1 summarizes the main characteristics of the tap water.

2.3. Coagulation–flocculation experiments

Experiments on dye coagulation and flocculation were performed using a jar test apparatus (Fisher-Bioblock, France). A standardized set of stirring speeds, i.e., 200 rpm for rapid stirring and 40 rpm for slow stirring, was used for comparative purposes (Roussy et al., 2005b). The initial pH of the solution was measured and then adjusted to a fixed value (depending on the experiments) using dilute HCl or NaOH solutions (0.01–0.1 M). The homogeneous dye solution was separated into several beakers, each containing 300 mL, to which various volumes of chitosan solution were added. The mixtures were then stirred at high velocity (200 rpm) for 3 min, after which the velocity was decreased to 40 rpm and maintained for 15 min. The stirring was then stopped and the experiments were performed at room temperature (i.e., $21 \text{ }^\circ\text{C} \pm 1.5 \text{ }^\circ\text{C}$). Following a settling time of 2 h, the samples were collected at the top of the settling beaker (the top 1 cm of the water phase) using a syringe. The collected samples were filtered through a $1.2 \text{ }\mu\text{m}$ Whatman filtration membrane (held on a filter support cartridge) and analyzed by means of UV-visible spectrophotometry (Shimadzu UV 160-A). The amount of dye retained on the membrane was negligible (less than 2%).

The quantity of dye on chitosan, q (in mg g^{-1} or mmol g^{-1}), was calculated according to the following mass balance equation: $q = V(C_0 - C_{\text{eq}})/m$, where V is the volume of solution (L); C_0 and C_{eq} are the initial and final dye concentrations (mg L^{-1} or mmol L^{-1}), respectively; and m (g) is the amount of chitosan added to the solution. The quantity of dye removed from the solution was assumed to be bound to the total amount of chitosan present.

2.4. Data analysis

The experimental data were analyzed statistically. The quality of the fitting of the parameters (in linear equations) was expressed by a correlation coefficient, and their statistical significance was analyzed by means of the Student's t -test. The level of significance was set at $p = 0.05$.

2.5. Image capture

For morphological observations, an optical microscope (Leitz, Laborlux 11, Germany) equipped with a video camera (Leica, DFC 420) and connected to a PC via a grabbing board was used. A drop of fresh mixed solution containing dye-chitosan flocs was carefully deposited on a glass slide and covered with a cover slip. The slide was observed immediately. Images were obtained at magnifications of $40\times$ and $10\times$.

3. Results and discussion

3.1. Effect of chitosan dosage, pH and type of water (tap or demineralized) on the coagulation–flocculation of AB92

The pH is a critical parameter in the efficiency of the coagulation–flocculation process. This parameter influences the solution properties (net charge of the dye) and the behavior of the biopolymer in the solution (charge of the amine groups). The addition of the chitosan to the dye solution changes the pH of the solution for two reasons: (a) the direct impact of the acidity of

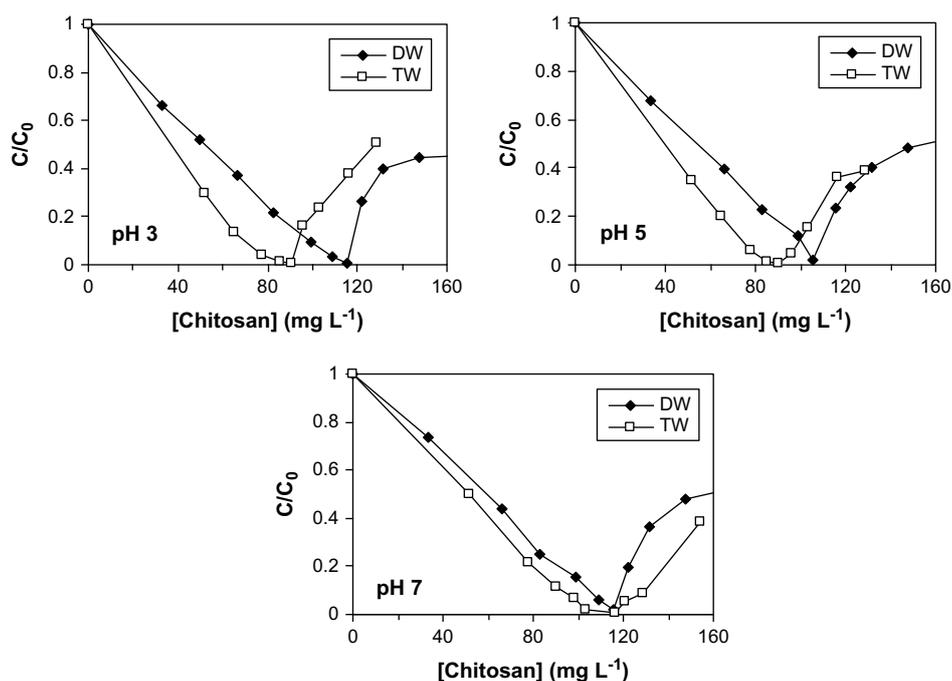


Fig. 3. Coagulation–flocculation of AB92 using demineralized water (DW) and tap water (TW) at pH levels of 3, 5 and 7. Dye concentration: 100 mg L^{-1} .

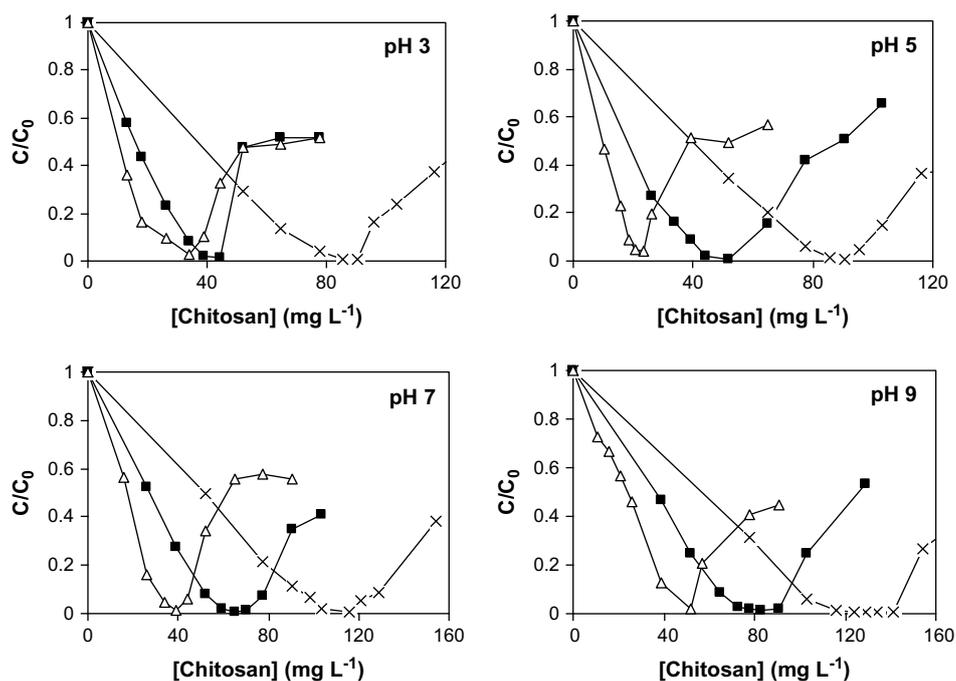


Fig. 4. Influence of initial pH, dye concentration and chitosan concentration on the coagulation–flocculation of AB92 with chitosan (\times : 100 mg L^{-1} ; \blacksquare : 50 mg L^{-1} ; \triangle : 25 mg L^{-1}).

the chitosan solution, and (b) the effect of the interaction of the dye with the biopolymer. Fig. 2 shows the pH variation resulting from the addition of increasing concentrations of chitosan. The pH change was significantly different for solutions prepared with tap water and with demineralized water. In the case of demineralized water, the equilibrium pH was almost the same ($\text{pH } 4.0 \pm 0.5$) regardless of the initial pH, and its value remained almost constant when chitosan concentration exceeded 50 mg L^{-1} . The addition of an acidic solution (the pH of the chitosan solution approached 3.0–4.0) into pure water (with weak ionic strength) substantially modified the pH of the solution. The pH of the solution was controlled by the acidic biopolymer solution. The trends are substantially different in the case of tap water. With a solution with a pH of 3.0, the pH increased continuously with increasing chitosan concentration until it reached 4.0. With a solution with a pH of 5, the equilibrium pH remained almost constant, regardless of the chitosan concentration. With a solution with a pH of 7, the final pH decreased with increasing chitosan concentration. The presence of salt in the tap water (i.e., higher ionic strength compared to demineralized water) limits the impact of the addition of chitosan solution on the final pH. In this case, it is possible to detect the impact of pH on the efficiency of the coagulation process. In the case of demineralized water, however, the pH variation is limited, so it is difficult to identify the impact of the pH on the treatment efficiency. Fig. 2 shows the effect of the chitosan dosage on the pH of the dye solution prepared with demineralized and tap water.

Fig. 2(a) shows that the addition of significant amounts of chitosan (dissolved in acetic acid solution) to the dye solution prepared with demineralized water significantly changed the pH of the final solution. At pH 3.0, the pH increased slightly (to 3.79), while at pH 5.0 and 7.0 the pH of the solution decreased to 3.98 and 4.23, respectively. This means that the final pH values were of the same order of magnitude for the experiments at pH 3.0 and pH 5.0.

However, some differences in the system pH of the dye solution prepared with tap water were observed. Fig. 2(b) shows that after

the addition of chitosan to the dye solution at an initial pH of 3.0, the pH increased slightly (to a final pH of 3.8). In the case of the dye solution with an initial pH of 5.0, the system pH remained constant even at high coagulant dosages (final pH of 5.1, chitosan dosage of 130 mg L^{-1}). In contrast, an increase in the coagulant dose at an initial pH of 7.0 was associated with a decrease in the solution pH (to a final pH of 5.5). As the coagulant amount increased, the pH decreased. The pH decrease indicates that the coagulation–flocculation of the dye solution with chitosan could be used to treat dye wastewaters that may have high pH values.

3.2. Interpretation of the coagulation–flocculation mechanism

Chitosan has reactive amino and hydroxyl groups that interact with negatively charged surfaces. The behavior of chitosan involves

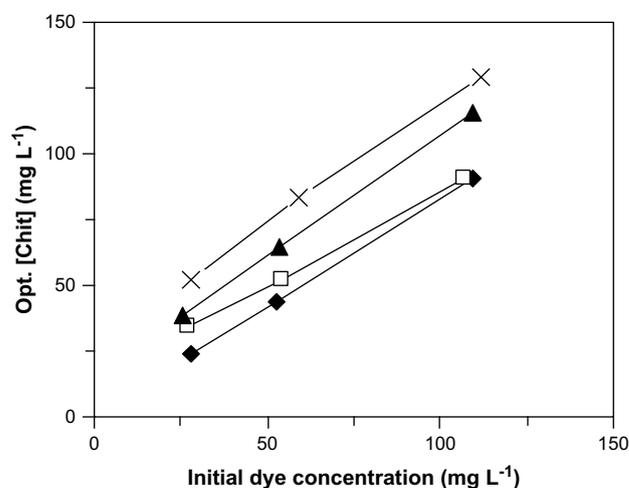


Fig. 5. Correlation between optimum chitosan dosage and initial dye concentration at pH levels of 3, 5, 7 and 9 (\blacklozenge : pH 3; \square : pH 5; \blacktriangle : pH 7; \times : pH 9).

Table 2

Correlation between optimum chitosan dosage and initial concentration of AB92 at pH levels of 3.0, 5.0, 7.0 and 9.0 in tap water.

pH _i	pH _{fin}	$\alpha \pm \sigma_\alpha$	$\beta \pm \sigma_\beta$	r	t_{cal}	$t_{0.95}$
3.0	3.5–3.7	0.82 ± 0.004	0.82 ± 0.15	0.9999	191.9	12.7
5.0	4.6–5.1	0.71 ± 0.014	14.3 ± 0.46	0.9998	51.3	12.7
7.0	6.0–6.8	0.92 ± 0.001	15.9 ± 0.03	0.9999	998.4	12.7
9.0	7.1–7.7	0.91 ± 0.034	27.6 ± 1.16	0.9993	27.1	12.7

Opt [Chit] = α [Dye]₀ + β .

σ_α and σ_β : standard deviations of α and β , respectively; r : estimated regression coefficient; t_{cal} : value of Student's t -test obtained from experimental results; $t_{0.95}$: value of Student's t -test set at a probability level of $p = 0.05$.

two factors, namely hydrophobic interactions and the possibility of chain association through hydrogen bridges. The hydrophobic interactions are due to the methyl group of the acetamide function and to the –CH and –CH₂ groups of the glucose ring. The H-bridges are usually generated by alcohol, amine, amide and ether functions on the chitosan chain. These chemical groups are implied in the competitive formation of both inter- and intramolecular H-bridges, as well as interactions with other substrates. Thus, the chemical behavior of chitosan varies according to the liquid media (Assaad et al., 2007).

Fig. 3 shows the coagulation–flocculation of AB92 solutions prepared with demineralized water and tap water with chitosan at pH levels of 3.0, 5.0 and 7.0. The coagulation–flocculation of this dye required lower amounts of chitosan with tap water than with demineralized water. This indicates that the ionic composition of the solution, possibly sulfate, had an important effect on the sorption of AB92 by chitosan or on the configuration of chitosan at the dye–water interface. It has been previously reported that chitosan appears to have a higher MW in the presence of sulfate (Barany and Szepesszentgyorgyi, 2004; Van Duin and Hermans, 1959). Van Duin and Hermans (1959) explained this observation with the hypothesis that chitosan formed larger aggregates and could precipitate in the presence of sulfate.

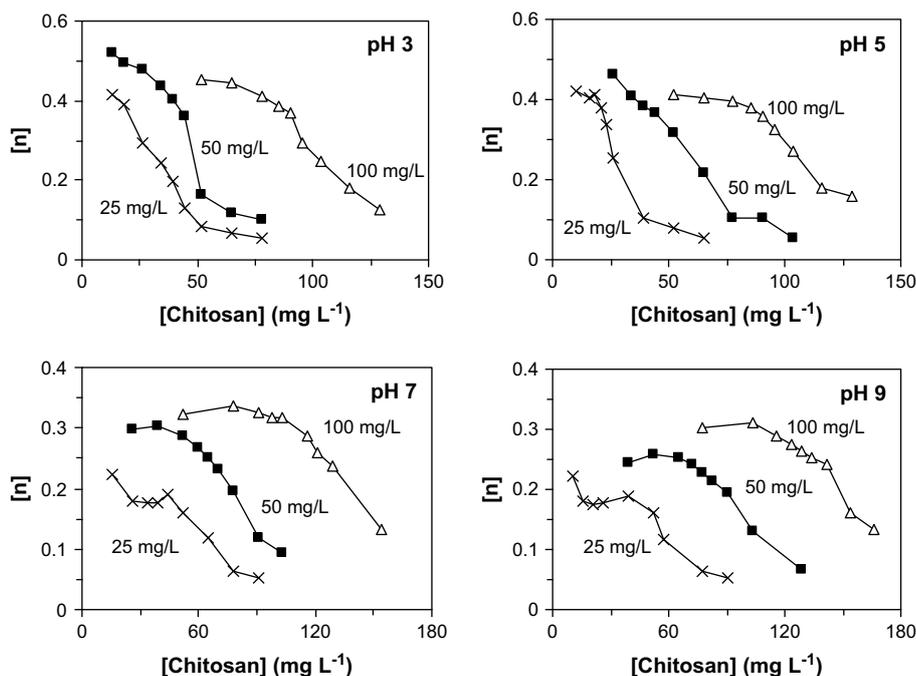


Fig. 6. Determination of the maximum molar ratio between the dye and amine groups ($[n]$, mol dye/mol amine groups of chitosan) in the coagulation–flocculation of AB92 at initial pH levels of 3, 5, 7 and 9.

3.3. Optimization of the coagulation–flocculation of AB 92 in tap water with chitosan

AB92 (prepared with tap water) was removed by means of coagulation–flocculation at pH levels of 3.0, 5.0, 7.0 and 9.0 for three different initial dye concentrations (25, 50 and 100 mg L⁻¹). The chitosan dosage was varied in order to determine the best coagulant dose for each dye concentration at various initial pH values (Fig. 4). As the chitosan dosage increased, the residual concentration of dye systematically reached a minimum before increasing again. These curves are typical of a coagulation–flocculation system controlled by a charge neutralization mechanism. The anionic dye bearing sulfonic groups is electrostatically attracted by the protonated amine groups of chitosan. This reaction neutralizes the anionic charges of dyes that can bind together and settle. When the protonated amine groups had completely neutralized the anionic charges, the dye removal reached its maximum. When the amount of chitosan added to the solution was increased, the excess protonated amine groups restabilized the suspension and decreased the efficiency of the process (Guibal and Roussy, 2007). The bridging mechanism is enhanced by the flocculating effect of the chitosan (due to its high MW) and by the interactions of the various anionic groups in the dye with the various protonated amine groups (inter- and intra-chain associations). Chitosan is involved in a dual mechanism that brings about coagulation by charge neutralization and flocculation by the bridging mechanism.

The effect of the initial dye concentration on the coagulation–flocculation process was also investigated, since dye concentration is an important parameter in wastewater treatment. The optimum concentration of chitosan (Opt [Chit]) versus initial dye concentration ([Dye]₀) was plotted (Fig. 5):

$$\text{opt[Chit]} = \alpha [\text{Dye}]_0 + \beta \quad (1)$$

Table 2 shows the parameters α and β and the correlation coefficients (r). These values, obtained with just three different initial dye

concentrations, can be taken as an indication of the order of magnitude of these parameters.

Changing the initial pH of the solution seemed to significantly change the performance of the system, i.e., different quantities of chitosan were required. At lower pH values, the amount of chitosan required for an efficient coagulation–flocculation of AB92 was lower than that needed at higher pH values. This can be explained by the acid–base properties of chitosan and the degree of dissociation of the polyelectrolyte (Guibal and Roussy, 2007). The pK_a of amine groups is close to 6.3–6.4 for fully dissociated chitosan (with a deacetylation degree of close to 90%). This means that at a pH of 5.0 or less, more than 90% of the amine groups are protonated. The initial pH of 3.0 obviously led to a more protonated form of chitosan. With a decrease in pH values, the dye protonation process could lead to a reduction in charge density and cause the dye molecules to self-aggregate. Therefore, less coagulant would be required to destabilize them. The short range of concentration for optimum dye removal increased with initial pH, which renders the process easier to control at a large scale.

The reliability of the correlation between optimum chitosan dosage and initial dye concentration was determined by the correlation coefficient. The statistical significance of the correlation was analyzed with the Student's t -test. By comparing the calculated t values (t_{cal}) with the Student's t values for a 95% confidence level ($t_{0.95}$), the variables were shown to be correlated ($t_{cal} > t_{0.95}$) (Table 2).

3.4. Optimum molar ratio between dye and amine groups

The residual concentrations found in the supernatant of the suspensions can be considered in the calculation of a virtual binding capacity (in mg of dye per g of chitosan or mmol of dye per g of chitosan). The mass balance equation is used and it is assumed that the total amount of chitosan added to the solution is available for interaction with the dye. It is also possible to calculate a conversion ratio between g of chitosan and mmol of amine groups; the water content of the chitosan flakes used to prepare the chitosan solution (i.e., approximately 10%) and the deacetylation degree (i.e., 87%) must be taken into account. These different conversion ratios were used to calculate the coefficient [n] (mol of dye/mol of amine groups) representing the molar conversion ratio at the optimum chitosan dosage. Fig. 6 shows the relationship between the coefficient [n] and chitosan dosage for the various initial dye concentrations. This coefficient ranged from 0.2 to 0.4 depending on the experimental conditions. The mean value for [n] was around 0.3. This ratio corresponds to a stoichiometry of 3:1 between the chitosan and the dye, which correlates well with the stoichiometry of the active groups in both the chitosan and the dye.

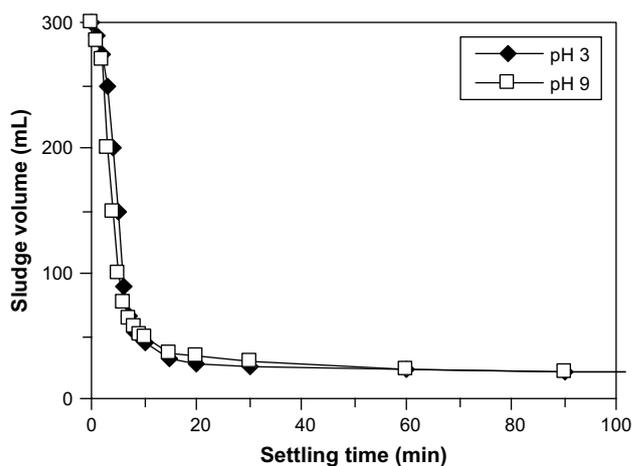


Fig. 7. Settling curves as a function of sludge volume under selected optimum conditions at initial pH levels of 3 and 9 (AB92 concentration: 100 mg L^{-1} ; chitosan dosage: 91 and 141 mg L^{-1} for pH levels of 3 and 9, respectively).

Indeed, the dye has three sulfonic groups per dye unit. Roberts (1992) used the dye/chitosan molar ratio to quantify chitosan in solution and Guibal and Roussy (2007) obtained similar results.

3.5. Sludge production

In general, the amount and characteristics of the sludge produced during the coagulation–flocculation process were highly dependent on the coagulant used and on the operating conditions (Amuda and Amoo, 2007). In order to evaluate this parameter, the optimum chitosan dosages were used for experiments performed with 100 mg L^{-1} of AB92 solution at pH levels of 3.0 and 9.0 (see previous sections). Once the experiment was performed in the jar test, the contents of the beakers were transferred to the Imhoff cone and the sludge production was determined by direct reading (mL of sludge produced for 300 mL of dye solution treated). Fig. 7 shows the results obtained using this method. Under selected conditions, the amount of sludge for both solutions was very low (22 mL of wet sludge per 300 mL of treated dye solution prepared at an initial pH of 3.0 and 9.0).

In the coagulation–flocculation process, the settling speed of the flocs is important, since this influences the overall cost and efficiency. Fig. 7 shows that considerable sludge reduction was achieved within 20 min of settling. This indicates that chitosan is very effective in removing dye and produces a small amount of sludge that settles very fast.

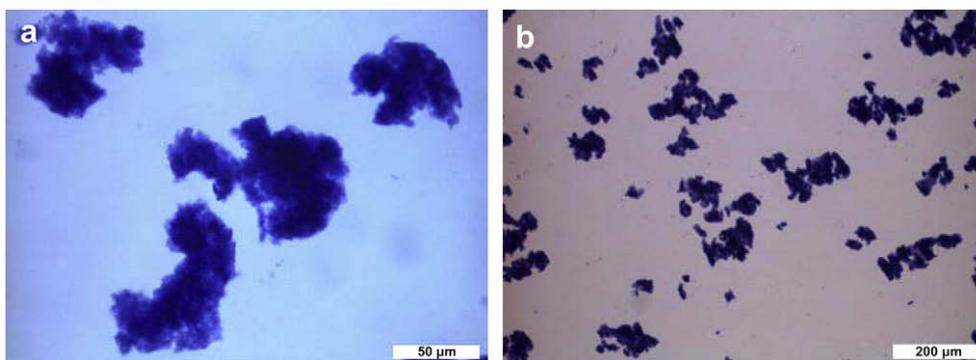


Fig. 8. Microscope photographs of flocs formed by chitosan: (a) single flocs and (b) floc aggregates.

3.6. Morphology of flocs

Floc size and structure are considered fundamental to the operation of industrial unit processes. In water and wastewater treatment processes, the aim is to remove impurities from water in the form of solid particles. Once the solid particles have been produced, they can be separated from the water by means of sedimentation, flotation, filtration and thickening techniques. The physical characteristics of flocs are therefore fundamental in determining their removal efficiency.

The evaluation and quantification of the structural characteristics of flocs are more difficult due to the highly irregular three-dimensional structure of flocs and their inherently delicate nature (Jarvis et al., 2005).

In Fig. 8, the heterogeneous nature and random dispersion of the components are clearly shown by the microscope photograph of flocs formed during coagulation–flocculation of AB92 solution with chitosan. Fig. 8(a) shows that single flocs had highly irregular shapes. Fig. 8(b) shows that floc aggregates (with diameters ranging from 100 to 200 μm) were dominant in number; this may explain the fast settling time.

3.7. Recovery of AB92 from dye-loaded flocs

The coagulation–flocculation process generally removed the dye very efficiently: over 99% of the AB92 was transferred to flocs. The AB92 was desorbed from the dye-loaded flocs in order to regenerate the spent chitosan and economize the coagulation–flocculation process. The desorption was performed in alkaline media in order to decrease the dye's affinity for chitosan: the deprotonation of amine groups disrupts the bonds between the amine groups and the anionic groups of the dye (i.e., sulfonic functions). Fig. 9 shows that AB92 was desorbed with sodium hydroxide (0.001–1 M) with 100% efficiency. The volume used for desorption studies was ten times smaller than that used for the coagulation–flocculation experiment. Thus, AB92 was not only effectively removed from the flocs but also concentrated. The recovered flocs were rinsed gently with water, dissolved in acetic acid solution (1%) and reused in a second coagulation–flocculation step. The efficiency of the dye removal in this step was 42%. This could be due to the loss of some flocs during their separation from the dye solution after centrifugation (by decantation). Due to the small amount of sludge produced during coagulation–flocculation with chitosan, it was not

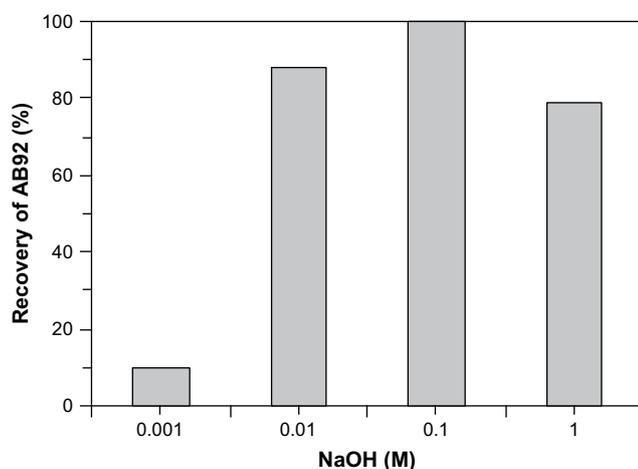


Fig. 9. Recovery of AB92 from dye-saturated flocs (coagulation–flocculation: initial dye concentration of 100 mg L^{-1} ; pH 3; chitosan dosage of 90 mg L^{-1} ; dye recovery conditions: 30 mL of NaOH, 15 min).

possible to optimize the reutilization of the recovered flocs. This topic is worthy of consideration in future studies.

4. Conclusions

This study has demonstrated that coagulation–flocculation of AB92 with chitosan is an effective method for clarifying dye wastewater. The results showed that lower amounts of chitosan were required for optimum removal when the dye was prepared in tap water than when it was prepared in demineralized water. Dye removal efficiency at various pH levels and dye concentrations was evaluated. The efficiency of coagulation–flocculation with tap water was shown to be highly dependent on the pH control and coagulant dose. At higher pH levels, larger amounts of chitosan were required to reach the maximum color removal of the treated solution. Chitosan can behave as a coagulant (charge neutralization) or as a flocculant (bridging), depending on the nature of the colloids, the pH of the suspension and the experimental conditions (i.e., concentrations). The respective contributions of these mechanisms also depend on the experimental conditions and on the characteristics of chitosan (i.e., its MW and degree of deacetylation). Decreasing the pH reduces the chitosan concentration required for optimum coagulation–flocculation. The results showed a very high degree of color removal ($\sim 99\%$ at optimal conditions). The use of chitosan as a coagulant in dye wastewater treatment resulted in a very low level of sludge production. The volume of the wet sludge at the bottom of the jar test beakers after the coagulation–flocculation process was used to quantify the volume of sludge generated in the study.

Very low doses of chitosan were needed for the destabilization and sedimentation of dye solutions. The settling time was short, and very low dye concentrations were obtained within a few minutes. These observations are consistent with the commercial use of chitosan for dye wastewater treatment.

It was possible to recover the chitosan from the dye-loaded flocs with 0.1 M NaOH (with a desorption efficiency of close to 100%).

Acknowledgments

This study was supported by the Spanish Ministry of Education and Science (ref. CTQ2005-09430) and the Department of Education and Universities of the Catalan Government (SGR2005-00934). A. Szyguła acknowledges the financial support of the Spanish Ministry of Education and Science. M. Ariño Palacín thanks the Socrates-Erasmus program for its economic support.

Appendix A. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jenvman.2009.04.002.

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